

Electronic Motion in the Rotating H<sub>2</sub> Molecule

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The contributions of the electrons in the H<sub>2</sub>-molecule to the moment of inertia is calculated by assuming irrotational flow for the motion of the electrons. Approximate expressions for the flow are obtained by means of a variational principle. It is found that the model accounts for at least 90% of the observed moment of inertia. Also the dependence of the moment of inertia on the internuclear spacing and the magnetic field of the electrons acting on the nuclei are calculated and found to be in rather good agreement with the experimental values.

## INTRODUCTION

RECENT high-precision measurements of the radio-frequency spectra of H<sub>2</sub>, HD, and D<sub>2</sub> have led to an accurate determination of certain molecular parameters associated with the effect of the rotation on the motion of the electrons.<sup>1-3</sup> Thus the so-called high-frequency term in the molecular magnetic susceptibility, which is directly related to the contribution of the electrons to the rotational moment of inertia, has been determined for zeroth vibrational, first and second rotational states. The magnetic field which acts on the nuclei as a consequence of the rotation of the electrons, has also been measured.

The rotational motion is close to that corresponding to the model of irrotational flow,<sup>4</sup> for which the moment of inertia is strongly dependent on the eccentricity of the electron density and vanishes for spherical symmetry. The irrotational flow model is exactly valid for a single electron in the lowest binding states in a rotating potential.<sup>4</sup> For the two electrons in the hydrogen molecule, the model remains valid in the approximation in which the electrons may be considered as moving independently in an average potential. We shall here attempt to calculate the molecular parameters on the basis of this approximation.

## EXPERIMENTAL RESULTS

The high-frequency term in the diamagnetic susceptibility  $\xi_{hf}$  is related to the rotational magnetic moment,<sup>5</sup> and is therefore a measurable quantity. It is assumed by Ramsey<sup>5</sup> that  $\xi_{hf}$  varies with the internuclear spacing  $R$  as  $R^l$ , that is

$$\xi_{hf} = F_e(R/R_e)^l, \quad (1)$$

where  $R_e$  is the internuclear spacing for a nonvibrating and nonrotating molecule. From measurements of the rotational magnetic moment in the first rotational states in H<sub>2</sub> and D<sub>2</sub>, or first and second rotational states

in H<sub>2</sub>, Ramsey *et al.* found<sup>1</sup>

$$\begin{aligned} \langle \xi_{hf} \rangle_1 &= (1.719 \pm 0.009) \times 10^{-31} \text{ erg gauss}^{-2} / \text{molecule}, \\ l &= 3.76 \pm 0.10. \end{aligned} \quad (2)$$

By using formulas given by Ramsey,<sup>5</sup> one finds, with this value of  $l$ :

$$\langle (R/R_e)^l \rangle_1 = 1.224 \pm 0.009. \quad (3)$$

Thus from (1) one obtains:

$$\begin{aligned} \xi_{hf}(R=R_e) &= F_e = (1.404 \pm 0.010) \\ &\times 10^{-31} \text{ erg gauss}^{-2} / \text{molecule}. \end{aligned} \quad (4)$$

The moment of inertia,  $\mathfrak{I}$ , is related to  $\xi_{hf}$  by

$$\mathfrak{I} = \frac{3}{2} (2mc/e)^2 \xi_{hf}, \quad (5)$$

and from (4) one then finds:

$$\mathfrak{I}_{\text{exp}} = (0.2703 \pm 0.0020) \times 10^{-44} \text{ erg sec}^2 / \text{molecule}. \quad (6)$$

The magnetic field  $H_N$  produced by the electrons at the position of one of the nuclei, is also measured in first rotational states in both H<sub>2</sub> and D<sub>2</sub>. Assuming

$$H_N = \Omega G_e(R/R_e)^m, \quad (7)$$

where  $\Omega$  is the angular velocity, Ramsey *et al.* find<sup>2</sup>

$$\left\langle \frac{H_N}{2I} \right\rangle_1 = (11.25 \pm 0.05) \text{ gauss}, \quad (8)$$

$$0.8 < m < 2.4, \quad \text{or} \quad -2.4 < m < -0.8,$$

where  $I$  is the rotational angular momentum. This gives

$$\frac{1}{2I} H_N(R=R_e) = (11.34 \pm 0.28) \text{ gauss}. \quad (9)$$

## THEORETICAL EXPRESSIONS

Since the molecule rotates very slowly compared with the motion of the electrons, the effect of rotation can be obtained by perturbation theory.

In a rotating coordinate system, we have

$$\{H - \Omega L_z\} \Psi = E \Psi, \quad (10)$$

where  $L_z$  is the component along the axis of the rotation of the total orbital angular momentum of all the

<sup>1</sup> Barnes, Bray, and Ramsey, Phys. Rev. **94**, 893 (1954).

<sup>2</sup> Harrick, Barnes, Bray, and Ramsey, Phys. Rev. **90**, 260 (1953).

<sup>3</sup> Kolsky, Phipps, Ramsey, and Silsbee, Phys. Rev. **87**, 395 (1952).

<sup>4</sup> G. C. Wick, Phys. Rev. **73**, 51 (1948).

<sup>5</sup> N. F. Ramsey, Phys. Rev. **87**, 1075 (1952).

electrons. Spin terms are not included since it is assumed that the spin orbit coupling may be neglected. To first order in  $\Omega$ , we then have

$$\Psi = \psi_0 + \sum_n' a_n \psi_n, \quad (11)$$

where

$$a_n = \Omega \langle 0 | L_z | n \rangle / (E_n - E_0). \quad (12)$$

$\psi_0$  and  $\psi_n$  represent ground and excited states of the nonrotating molecule.

The increase in energy caused by the rotation is

$$\Delta E = E_{\text{rot}} = \frac{1}{2} \mathfrak{I} \Omega^2, \quad (13)$$

with

$$\mathfrak{I} = 2 \sum_n' \frac{|\langle 0 | L_z | n \rangle|^2}{E_n - E_0}. \quad (14)$$

For the magnetic field  $H_N$  produced by the rotating electrons at the nucleus, we have

$$\begin{aligned} H_N &= -\frac{1}{c} \int \frac{\mathbf{r} \times \mathbf{j}}{r^3} d\tau \\ &= \frac{\Omega e}{mc} \sum_n' \frac{\langle 0 | L_z | n \rangle \langle n | L_z / r^3 | 0 \rangle + \langle 0 | L_z / r^3 | n \rangle \langle n | L_z | 0 \rangle}{E_n - E_0}, \end{aligned} \quad (15)$$

where the origin of  $\mathbf{r}$  is the nucleus at which the magnetic field is determined, and  $\mathbf{j}$  is the electron current density.

#### POTENTIAL FLOW APPROXIMATION

We introduce a density distribution

$$\rho(\mathbf{r}) = m \int \psi_0^2 \sum_i \delta(\mathbf{r} - \mathbf{r}_i) d\tau \quad (16)$$

for the ground state, and a velocity field given by the equations

$$\nabla \rho \mathbf{V} - \Omega \partial \rho / \partial \varphi = 0, \quad (17)$$

$$\nabla \times \mathbf{V} = 0. \quad (18)$$

For this potential flow, the energy of rotation is given by

$$E_{\text{rot}} = \frac{1}{2} \int \rho \mathbf{V}^2 d\tau = \frac{1}{2} \mathfrak{I}_{\text{irr}} \Omega^2, \quad (19)$$

where  $\mathfrak{I}_{\text{irr}}$  is defined by the last equation.

Moreover, for the magnetic field  $H_N$  produced by this flow, one obtains

$$(H_N)_{\text{irr}} = \frac{e}{mc} \int \frac{\mathbf{r} \times \rho \mathbf{V}}{r^3} d\tau. \quad (20)$$

#### (a) One Electron

Suppose for a moment that there is only one electron. The current density, to first order in  $\Omega$ , is then given by

$$\mathbf{j} = (i\hbar/m) \sum_n a_n \{ \psi_0 \nabla \psi_n - \psi_n \nabla \psi_0 \}, \quad (21)$$

where  $\psi_0$  and  $\psi_n$  are assumed to be real. Since the ground state wave function  $\psi_0$  has no nodes, we may introduce<sup>4</sup> the velocity field

$$\mathbf{V} = \mathbf{j} / \rho, \quad (22)$$

where  $\rho$  is the density (16). As is easily seen,  $\mathbf{V}$  satisfies both Eqs. (17) and (18). Moreover, if we use this expression for  $\mathbf{V}$  in (19) and (20) and compare the result with (14) and (15), the result will be

$$\mathfrak{I} = \mathfrak{I}_{\text{irr}}, \quad H_N = (H_N)_{\text{irr}}.$$

In this case, therefore, the potential flow model has exact validity.<sup>4</sup>

#### (b) Two Electrons

For a system of two electrons in the ground state, it is possible to show that

$$\mathfrak{I} > \mathfrak{I}_{\text{irr}}. \quad (23)$$

To see this, we introduce

$$\begin{aligned} \mathbf{j}_1(\mathbf{r}_1, \mathbf{r}_2) &= \frac{i\hbar}{2m} \{ \Psi^*(\mathbf{r}_1, \mathbf{r}_2) \nabla_1 \Psi(\mathbf{r}_1, \mathbf{r}_2) - \Psi(\mathbf{r}_1, \mathbf{r}_2) \nabla_1 \Psi^*(\mathbf{r}_1, \mathbf{r}_2) \} \\ &= -\frac{i\hbar}{m} \sum_n' a_n \{ \psi_0(\mathbf{r}_1, \mathbf{r}_2) \nabla_1 \psi_n(\mathbf{r}_1, \mathbf{r}_2) \\ &\quad - \psi_n(\mathbf{r}_1, \mathbf{r}_2) \nabla_1 \psi_0(\mathbf{r}_1, \mathbf{r}_2) \}. \end{aligned} \quad (24)$$

Since  $\psi_0$  is always different from zero, we may also define

$$\mathbf{V}_1(\mathbf{r}_1, \mathbf{r}_2) = \mathbf{j}_1 / \rho',$$

where

$$\rho'(\mathbf{r}_1, \mathbf{r}_2) = m \psi_0^2(\mathbf{r}_1, \mathbf{r}_2).$$

By comparing the result with (19), one sees that

$$\mathfrak{I} \Omega^2 = \int \rho' \mathbf{V}_1^2 d\tau_1 d\tau_2 = \int \frac{\mathbf{j}_1^2}{m \psi_0^2} d\tau_1 d\tau_2. \quad (25)$$

Using Schwarz's inequality, we find

$$\int \frac{\mathbf{j}_1^2}{\psi_0^2} d\tau_2 \int \psi_0^2 d\tau_2 \geq \left( \int \mathbf{j}_1 d\tau_2 \right)^2, \quad (26)$$

and from (25) it thus follows that

$$\mathfrak{I} \Omega^2 \geq \int d\tau_1 \frac{\left( \int \mathbf{j}_1 d\tau_2 \right)^2}{m \int \psi_0^2 d\tau_2} = \int \frac{\mathbf{j}^2(\mathbf{r}_1)}{\rho(\mathbf{r}_1)} d\tau_1 \quad (27)$$

where  $\rho$  is defined by (16), and where

$$\mathbf{j}(\mathbf{r}_1) = \int \mathbf{j}_1(\mathbf{r}_1, \mathbf{r}_2) d\tau_2 \quad (28)$$

is the usual current density. If we write

$$\mathbf{V}' = \mathbf{j}/\rho, \quad (29)$$

we get from (27)

$$\mathfrak{I}\Omega^2 \geq \int \rho V'^2 d\tau. \quad (30)$$

It is easy to see that  $\mathbf{V}'$  satisfies (17), but that

$$\nabla \times \mathbf{V}' = \mathbf{a}.$$

We may divide  $\mathbf{V}'$  in two parts,  $\mathbf{V}$  and  $\mathbf{V}''$ , where  $\mathbf{V}$  is the potential flow satisfying (17) and (18) and where

$$\nabla \rho \mathbf{V}'' = 0, \quad \nabla \times \mathbf{V}'' = \mathbf{a}.$$

Substituting this into (30), we get

$$\mathfrak{I}\Omega^2 \geq \int \rho (\mathbf{V} + \mathbf{V}'')^2 d\tau = \int \rho V^2 d\tau + \int \rho V''^2 d\tau > \int \rho V^2 d\tau,$$

and thus

$$\mathfrak{I} > \mathfrak{I}_{\text{irr}}.$$

If the electrons can be considered as moving independently, so that  $\psi$  is a product wave function, one gets the exact result

$$\mathfrak{I} = \mathfrak{I}_{\text{irr}} \quad \text{and} \quad \mathbf{a} = 0.$$

The magnetic field  $H_N$  is that produced by the total velocity field  $\mathbf{V}'$  [see (29)], and  $(H_N)_{\text{irr}}$  represents the part which is caused by the irrotational part of this field.

In the case of more than two electrons, the ground state wave function possesses nodes, and the rotational motion is then in general essentially different from that of the potential flow model. In the limit of many particles moving independently in a rotating field, it may be shown that for the ground state the moment of inertia approaches that corresponding to rigid rotation.<sup>6</sup>

#### VARIATIONAL PRINCIPLE

If, in accordance with (18), we put  $\mathbf{V} = -\nabla\phi$ , the velocity potential  $\phi$  is given as a solution of the equation

$$\nabla(\rho\nabla\phi) + \Omega\partial\rho/\partial\varphi = 0. \quad (31)$$

TABLE I. Calculation of  $\mathfrak{I}_{\text{irr}}$  using Nordsieck's wave function. The trial function has the form  $\phi_{\text{trial}} = C_1xy + C_2xy^3 + C_3x^3y + C_4xy^5$ . The table shows the result obtained by including one, two, three, and four terms in this trial function.  $R = 1.4a_H$ .

$C_1/\Omega$	$C_2/\Omega R^{-2}$	$C_3/\Omega R^{-2}$	$C_4/\Omega R^{-4}$	$\mathfrak{I}_{\text{irr}}$ atomic units	$\mathfrak{I}_{\text{irr}}$ erg sec <sup>2</sup> molecule
0.1513				0.07963	$0.2088 \times 10^{-44}$
0.1815	-0.01646			0.08534	$0.2174 \times 10^{-44}$
0.1955	-0.01493	-0.01126		0.08750	$0.2228 \times 10^{-44}$
0.2097	-0.02851	-0.01094	0.001504	0.08930	$0.2274 \times 10^{-44}$

<sup>6</sup> A. Bohr and B. Mottelson, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. 30, No. 1 (1955).

In order to find an approximate solution of (31), we introduce a variational principle.<sup>7</sup>

Defining

$$I = \int \left\{ \Omega \rho \frac{\partial}{\partial \varphi} \phi + \frac{1}{2} \rho (\nabla \phi)^2 \right\} d\tau, \quad (32)$$

we get by partial integration and use of (31)

$$\mathfrak{I}_{\text{irr}} \Omega^2 = -2I. \quad (33)$$

As is easily seen,  $\delta \mathfrak{I}_{\text{irr}} = 0$  for first-order variations of  $\phi$  around a solution to (31). If we put  $\phi_{\text{trial}} = \phi + \phi'$ , where  $\phi$  is an exact solution of (31), we get from (32)

$$I_{\text{trial}} = I_{\text{exact}} + \frac{1}{2} \int \rho (\nabla \phi')^2 d\tau.$$

It thus follows that the moment of inertia obtained from (32) and (33) by using a trial velocity potential, is always smaller than the exact irrotational value,

TABLE II. Calculation of  $\mathfrak{I}_{\text{irr}}$  using Nordsieck's wave function and the trial function:  $\phi_{\text{trial}} = C_1xy + C_2xy^3 + C_3x^3y$ .  $R = 1.4a_H$ .

$C_1/\Omega$	$C_2/\Omega R^{-2}$	$C_3/\Omega R^{-2}$	$\mathfrak{I}_{\text{irr}}$ atomic units	$\mathfrak{I}_{\text{irr}}$ erg sec <sup>2</sup> molecule
0.1867	-0.01591	-0.01246	0.08613	$0.2193 \times 10^{-44}$

that is,

$$\mathfrak{I}_{\text{irr}}^{\text{trial}} < \mathfrak{I}_{\text{irr}}^{\text{exact}}.$$

#### NUMERICAL RESULTS

As trial function we have chosen

$$\phi_{\text{trial}} = C_1xy + C_2xy^3 + C_3x^3y + C_4xy^5 + \dots, \quad (34)$$

which satisfies the symmetry properties required by (31). To obtain the electron density distribution, we first employ the wave function suggested by Nordsieck.<sup>8</sup> The result of the calculation is shown in Table I, for an internuclear spacing  $R$ , equal to the equilibrium value  $1.4a_H$  where  $a_H$  is Bohr's radius.

As is seen from (34), we have omitted all terms containing  $z$ . To justify this, we have also performed the calculation using

$$\phi_{\text{trial}} = C_1xy + C_2xy^3 + C_3z^2xy.$$

The result is given in Table II, and it is seen that the contribution from this new term is small compared with the contributions from  $x^3y$  and  $xy^5$ .

We have also carried out the calculations using a ground state wave function introduced by Newell.<sup>9</sup> The result is given in Table III.

<sup>7</sup> This variational principle was suggested to us by Professor F. J. Dyson.

<sup>8</sup> A. Nordsieck, Phys. Rev. 58, 310 (1940).

<sup>9</sup> G. F. Newell, Phys. Rev. 78, 711 (1950).

Of the two wave functions used, Newell's seems to be the better one, first, because it gives a better dissociation energy (Nordsieck: 4.0 ev; Newell 4.5 ev; Exp.: 4.72 ev), secondly, because it gives a better value of the quadrupole moment  $Q_e$  of the electron distribution. For this quantity, Nordsieck's and Newell's wave functions give the values  $1.057a_H^2$  and  $1.082a_H^2$ , respectively, while the very accurate wave function of James and Coolidge<sup>10</sup> leads to the value  $Q_e=1.076a_H^2$ , which is in good agreement with the experimental value.

The importance of  $Q_e$  for the present purpose is seen from the fact that if we use only the first term of the trial function (34), we get

$$\mathfrak{J}_{\text{irr}}^{\text{trial}} = \frac{1}{4} \frac{Q_e^2}{\langle x^2 + y^2 \rangle}. \quad (35)$$

Thus the best value of  $\mathfrak{J}_{\text{irr}}^{\text{trial}}$  is that obtained from Newell's wave function, which gives (see Table III).

$$\mathfrak{J}_{\text{irr}}^{\text{trial}} = 0.2422 \times 10^{-44} \frac{\text{erg sec}^2}{\text{molecule}}. \quad (36)$$

Since  $\mathfrak{J}_{\text{irr}}^{\text{trial}}$  represents a lower limit of  $\mathfrak{J}_{\text{irr}}$ , we conclude that the potential flow approximation accounts for at least 90% of the actual moment of inertia  $\mathfrak{J}$ , given by (6).

As seen from Table III, we have performed the calculation of  $\mathfrak{J}_{\text{irr}}$  for three values of  $R$  ( $R=1.3a_H$ ,  $1.4a_H$ , and  $1.5a_H$ ), using Newell's wave function. From these results we obtain for the exponent in (1)

$$l=3.40, \quad (37)$$

which is to be compared with the experimental value  $l=3.76$ .

It is instructive to consider the behavior of  $\mathfrak{J}$  in the two limits of  $R \ll a_H$  and  $R \gg a_H$ . In the latter limit, the potential flow model gives the rigid moment of inertia, and thus  $\mathfrak{J} \sim R^2$ . For  $R \ll a_H$ , the molecule resembles a He atom with a nuclear quadrupole moment. Considering the combined effect of the quadrupole field and the rotational perturbation  $\Omega L_z$ , one finds from a fourth-order perturbation calculation  $\mathfrak{J} \sim R^4$ . A quantitative calculation of  $\mathfrak{J}$  in this region is made difficult by the necessity to take into account the mutual screening effect of the electrons.

The fact that the observed value of  $l$  is rather close to the value for  $R \ll a_H$ , is consistent with the fact that  $\mathfrak{J}_{\text{obs}} \ll \mathfrak{J}_{\text{rig}}$ , and is connected with the small eccentricity of the electron density distribution in the hydrogen molecule.

<sup>10</sup> H. M. James and A. S. Coolidge, *Astrophys. J.* **87**, 447 (1938).

TABLE III. Calculation of  $\mathfrak{J}_{\text{irr}}$  using Newell's wave function and the trial function:  $\phi_{\text{trial}} = C_1xy + C_2xy^3 + C_3x^3y + C_4xy^5$ . The calculations are performed for three values of the internuclear spacing.

$R=1.3a_H$				$\mathfrak{J}_{\text{irr}}$ atomic units	$\mathfrak{J}_{\text{irr}}$ erg sec <sup>2</sup> molecule
$C_1/\Omega$	$C_2/\Omega R^{-2}$	$C_3/\Omega R^{-2}$	$C_4/\Omega R^{-4}$		
0.1472				0.07028	$0.1790 \times 10^{-44}$
0.1781	-0.01487			0.07619	$0.1941 \times 10^{-44}$
0.1937	-0.01322	-0.01102		0.07892	$0.2010 \times 10^{-44}$
0.2006	-0.01996	-0.01070	0.0007112	0.07966	$0.2029 \times 10^{-44}$
$R=1.4a_H$				$\mathfrak{J}_{\text{irr}}$ atomic units	$\mathfrak{J}_{\text{irr}}$ erg sec <sup>2</sup> molecule
$C_1/\Omega$	$C_2/\Omega R^{-2}$	$C_3/\Omega R^{-2}$	$C_4/\Omega R^{-4}$		
0.1560				0.08443	$0.2150 \times 10^{-44}$
0.1880	-0.01701			0.09071	$0.2310 \times 10^{-44}$
0.2039	-0.01536	-0.01243		0.09348	$0.2381 \times 10^{-44}$
0.2172	-0.02777	-0.01221	0.001353	0.09511	$0.2422 \times 10^{-44}$
$R=1.5a_H$				$\mathfrak{J}_{\text{irr}}$ atomic units	$\mathfrak{J}_{\text{irr}}$ erg sec <sup>2</sup> molecule
$C_1/\Omega$	$C_2/\Omega R^{-2}$	$C_3/\Omega R^{-2}$	$C_4/\Omega R^{-4}$		
0.1734				0.1105	$0.2814 \times 10^{-44}$
0.2092	-0.02075			0.1187	$0.3023 \times 10^{-44}$
0.2250	-0.01879	-0.01405		0.1218	$0.3103 \times 10^{-44}$
0.2396	-0.03375	-0.01363	0.001791	0.1238	$0.3155 \times 10^{-44}$

As to  $(H_N)_{\text{irr}}$ , we have performed the calculation by employing Nordsieck's wave function and including only the first term in the trial function (34). The result is

$$(H_N/2I)_{\text{irr}}^{\text{trial}} = 9.8 \text{ gauss}, \quad (38)$$

which is to be compared with the experimental value  $H_N/2I = 11.34$  gauss given by (9). The agreement must be considered as rather satisfactory since  $H_N$  is not calculated by a variational principle.

As seen from (8), the experimental value of  $m$  is rather uncertain. It is also here instructive to consider the behavior of  $H_N$  in the limits  $R \ll a_H$  and  $R \gg a_H$ . In the latter  $H_N \sim \Omega R^{-1}$ . In the limit  $R \ll a_H$ , one can obtain some information by using perturbation calculation on the helium atom. Since second-order terms will give a contribution because of the factor  $r^3$ , which appears in the formulas for  $H_N$  [see (15)], one gets  $H_N \sim \Omega R^2$ ; that is,  $m=2$ . One would expect, therefore, an experimental value of  $m$  between  $-1$  and  $2$ , and rather close to  $2$ , which is consistent with the experimental results.

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